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REPLY TO ATTN OF: GP

OCT 15 1973

TO: KSI/Scientific & Technical Information Division
Attention: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General Counsel for Patent Matters

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures agreed upon by Code GP and Code KSI, the attached NASA-owned U.S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No.	: 3,334,225
Government or Corporate Employee	: Cal/Tech Pasadena, CA
Supplementary Corporate Source (if applicable)	: JPL
NASA Patent Case No.	: XNP-04231

NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:
Yes [X] No [ ]
Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of column No. 1 of the Specification, following the words ". . . with respect to an invention of . . ."

Elizabeth A. Carter

Elizabeth A. Carter
Enclosure
Copy of Patent cited above

Aug. 1, 1967

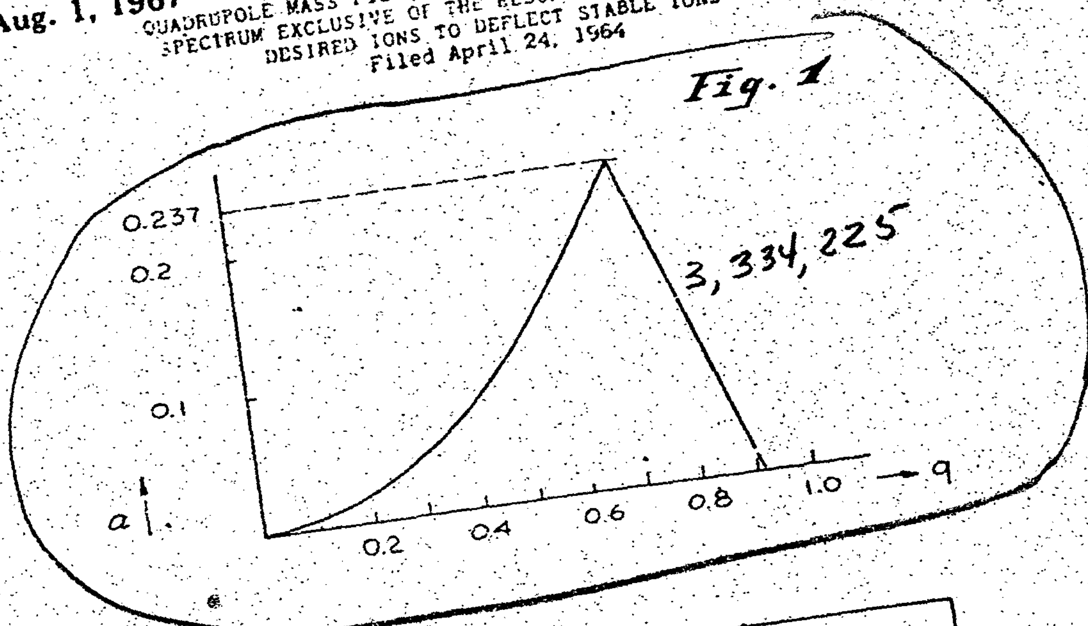
R. V. LANGMUIR

3,334,225

QUADRUPOLE MASS FILTER WITH MEANS TO GENERATE A NOISE SPECTRUM EXCLUSIVE OF THE RESONANT FREQUENCY OF THE DESIRED IONS TO DEFLECT STABLE IONS

Filed April 24, 1964

Fig. 1



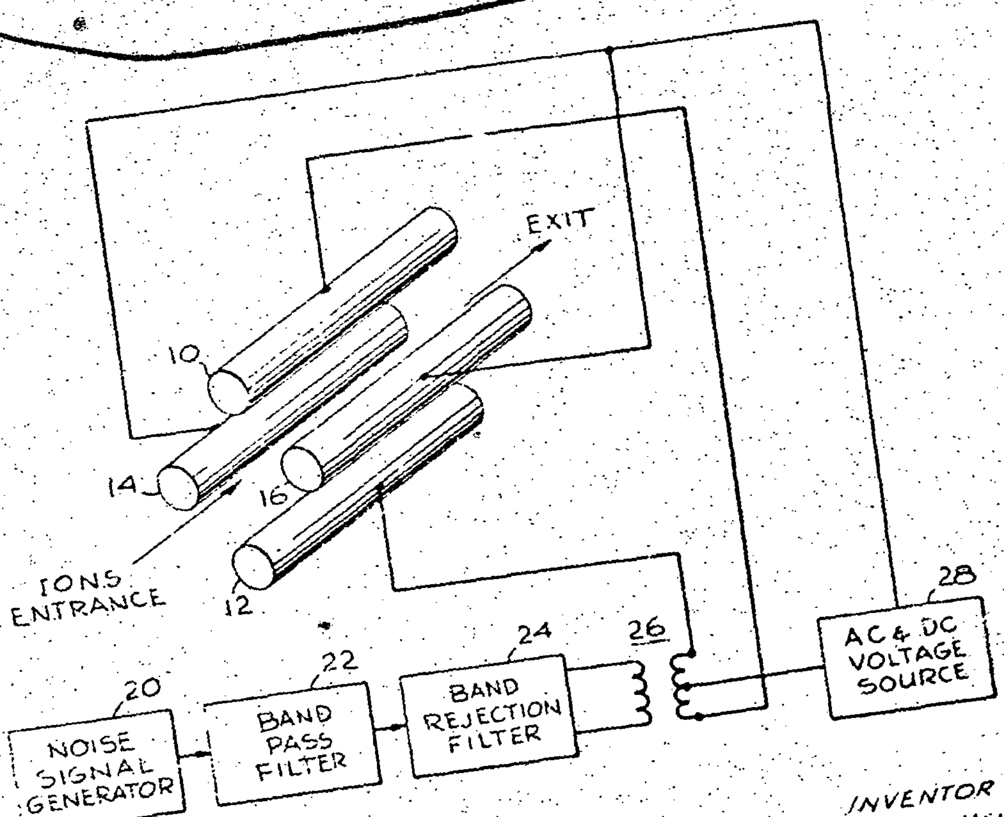


Fig. 2

INVENTOR
ROBERT V. LANGMUIR
BY Samuel Lindenberg
ATTORNEY

(NASA-Case-XNP-04231) QUADRUPOLE MASS FILTER WITH MEANS TO GENERATE A NOISE SPECTRUM EXCLUSIVE OF THE RESONANT FREQUENCY OF THE DESIRED IONS TO DEFLECT (Jet Propulsion Lab.) 4 p CSCL 14B N73-32325 Unclas 00/14 18073

United States Patent Office 3,334,225 Patented Aug. 1, 1967

3,334,225

QUADRUPOLE MASS FILTER WITH MEANS TO GENERATE A NOISE SPECTRUM EXCLUSIVE OF THE RESONANT FREQUENCY OF THE DESIRED IONS TO DEFLECT STABLE IONS

Robert V. Langmuir, Altadena, Calif., assignor to California Institute Research Foundation, Pasadena, Calif., a corporation of California

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5 Claims. (Cl. 250—41.9)

This invention relates to mass spectrometers of the type used for the separation or separate indication of ions of different specific electric charges, and more particularly to an improved method and means for the operation thereof.

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 426; 42 U.S.C. 2451), as amended.

In Patents 2,939,952 and 2,950,389, both to W. Paul et al., there is described both the theory and construction of a mass spectrometer. This instrument has an analyzing section into which ions are injected. In this analyzing section, a periodically varying electric field is established by applying both DC and AC potentials to electrodes which may be four circular rods extending parallel to one another and positioned 90 degrees apart. The ions, which are injected substantially axially into the cylindrical region effectively defined by the four circular rods, are excited by the periodically varying field to perform oscillations while traveling axially, along trajectories which are either stable or unstable depending upon a number of parameters including the frequency of the field and the specific electric charges on the respective ions. The specific charge of the ion has been defined as e/m, where e is the electric charge and m the mass of the particles. The ions that follow a stable trajectory pass through the electric field to a collector electrode or other target, whereas the ions following unstable trajectories impinge upon the laterally located electrodes or rods that produce the electric field, thus being prevented from reaching the target. In this manner, the desired isotope separation or separate indication is obtained.

As described in these patents, a periodic function which is applied to the electrodes to produce a periodically varying electric field may be produced by applying a sinusoidal oscillation superimposed upon a DC voltage which comprises a constant finite value. As a result of the field established, there are produced stable ranges in which the oscillation amplitude of ions of a given specific electric charge does not exceed the given maximum value. Hence, only such ions can pass from an ion source, axially between the electrodes and then out to the target. The other ions, having different specific electric charges and performing unstable oscillations after entering the periodically electric field, assume oscillation amplitudes of such large magnitude as to impinge upon the electrodes.

It has been further taught in these patents that a narrow unstable range can be embedded in a wide stable range by superimposing upon a rotationally symmetrical high frequency field another alternating field of smaller amplitude or potential whose frequency is one-half of that of the high frequency field. This is supposed to afford a separation of ions of a given charge out of an isotope mixture.

Also taught in these patents is that two or more isotopes or ions of respectively different specific charges may be separated from an isotope mixture by passing a flow of these isotopes through a periodic high frequency field, substantially as described, but with a superimposition thereon of another alternating field whose frequency

is adjusted to a selected working point within a stable range. This extra field is essentially a uniform electric field, such as might be obtained by placing a voltage source between opposite electrodes. More specifically, the superimposed additional alternating field is given a frequency which coincides, at least approximately, with the fundamental or upper harmonic oscillation of ions having a predetermined specific charge, thus enforcing unstable paths for these particular ions. It is also taught that the fundamental oscillation frequency of ions of a given specific electric charge traveling through an electric field comprised of a constant unidirectional component and a periodically variable high frequency component, depends not only upon the electric charge of the ions but also upon the magnitude of the field-producing direct-voltage, the amplitude of the field-producing high frequency, the magnitude of the high frequency itself, and also upon the geometry of the field-producing electrodes.

In the operation of the mass spectrometer, it has been found that it is necessary to carefully control the initial transverse velocity and displacement of ions which are injected into the field of the quadrupole structure, otherwise the accuracy of the results obtained are affected.

An object of this invention is to provide a novel method and means of operating a mass spectrometer whereby a larger variation on initial transverse velocity and displacement of ions being injected into the quadrupole structure is permitted than those used with present techniques.

Yet another object of the present invention is to provide a novel method and means for operating a mass spectrometer of the type described.

Still another object of the present invention is the provision of an improved method and means for operating a mass spectrometer of the type described.

These and other objects of the invention are achieved, by applying electrical signals to the quadrupole field-establishing electrodes, which signals effectively constitute a noise spectrum having a power spectral distribution which has a notch in the region for which a desired ion is resonant. As a result, all ions are rejected by the noise voltage except the desired ion, which passes through the quadrupole structure relatively uninfluenced by the noise voltage.

The novel features that are considered characteristic of this invention are set forth with particularity in the appended claims. The invention itself both as to its organization and method of operation, as well as additional objects and advantages thereof, will best be understood from the following description when read in connection with the accompanying drawings, in which:

FIGURE 1 is a stability diagram for this type of mass spectrometer, and

FIGURE 2 is a block schematic diagram showing an arrangement for biasing the quadrupole electrodes in accordance with this invention.

In FIGURE 1 is shown a stability diagram for a symmetrical electrode arrangement of the type which is employed in the mass spectrometer, of the type described, whose symmetry axis constitutes the x axis. The magnitudes a and q represented by the coordinate axes of the diagram, determine the working point of the device. The derivation of the a and q terms is shown in Patents 2,939,952 and 2,950,389 to Paul et al. In an article by Jay Schaefer and M. H. Nichols entitled, "Mass Spectrometer for Upper Air Measurement," which was published in the A.R.S. Journal, December 1961, p. 1773, it is shown that a region in which the ion trajectory is stable occurs when the following is satisfied: $a/q=2U/2V$, where V is the peak value of an RF sine wave upon which is superimposed the DC voltage U.

Referring now to FIGURE 2, there is shown a schematic-block diagram in accordance with this invention. The mass spectrometer structure is shown and described in detail in the previously referred to patents and article, and therefore, will not be redescribed here. What is shown in FIGURE 2 is a schematic representation of the quadrupole electrode arrangement comprising cylindrical rods 10, 12, 14, 16. These are spaced from each other at 90 degrees, are enclosed in an evacuated vessel (not shown). Ions to be analyzed are injected at one end of an imaginary cylindrical figure defined by these electrodes. These ions proceed down the x axis, which is the cylindrical axis thereof. Those of these ions which are not withdrawn by the electric field which is established between the quadrupole electrode are captured by a target (not shown), at the exit side of the electrode.

As explained in detail in the references indicated above, for certain DC and AC voltages which are applied to the quadrupole electrodes, only ions of a given e/m will pass through to the target. This results, as explained in these references, because operation is at such a point in the a–q diagram that, for instance, vertical motion is stable for ions of e/m above a certain value and for horizontal motion ions below a certain value of e/m are stable. These two values of e/m are chosen (by choosing proper values of a and q) to be close together and so to pass only ions having the desired e/m. It should be noted that for both vertical and horizontal motion, the a–q operation point is quite close to the limit of instability and that consequently the ions undergo quite large excursions. Thus, for a given maximum permissible excursion, the allowable transverse velocity and displacement on entrance is quite limited.

It is shown and described in the above-indicated references that if a small AC voltage is applied between electrodes 10 and 12 in FIGURE 2, an ion of a given e/m will have its amplitude increased as if it were in resonance. This resonant frequency is given by $\beta r/2$ where r is the angular frequency of the main quadrupole AC drive and β is a number between 0 and 1 which depends on the value of a and q at which operation takes place. For instance, if $a=0$ and $q=⅔$, β equals ½ approximately. At these values of a and q, the ions would be very strongly contained in the quadrupole system in the absence of any drive between electrodes 10 and 12, since operation is not near an unstable region in the a–q diagram. Where $a=0$, the relation between β and q is displayed in an article entitled "Electrodynamic Containment of Charge Particles" by Wuerker, Shelton, and Langmuir, which was published in the Journal of Applied Physics, vol. 30, No. 3, pp. 342 through 349 in March 1959.

In accordance with this invention, an ion is permitted to pass through the field established by the quadrupole electrodes by applying across electrodes 10 and 12, FIGURE 2, a noise spectrum having a power spectral distribution which has frequency components corresponding to 0 less than β, less than 1 $(0<\beta<1)$, except just near that frequency for which the desired ion is resonant (say near $\beta=½$). In this way, all ions are rejected by the noise voltage except the desired ions, which pass through the quadrupole structure relatively uninfluenced by the noise voltage, since no components of the noise voltage lie near the resonant frequency of the desired ion.

Referring again to FIGURE 2, a noise signal generator 20 provides a broad noise spectrum. The range of the noise spectrum which it is desired to use is determined by a band pass filter 22 to which the output of the noise signal generator 20 is applied. The portion of the noise spectrum which it is desired to reject, within the range provided at the output of the band pass filter 22, is determined by a band rejection filter 24, to which the output of the band pass filter is applied. The output of the band rejection filter is applied to the primary of the transformer 26. The secondary of the transformer has a center tap. The outer ends of the secondary winding are connected to the opposed electrodes 10, 12. A small AC voltage superimposed on a DC voltage is provided by a source 28. The output of the source 28 is applied to the two electrodes 14, 16, and also via the center tap of the secondary winding of the transformer 26 to the electrodes 10, 12.

It is shown in an article by Paul, Reinhard and Von Zahn, which is published in the Zeitschrift fur Physik, p. 152, vol. 143, published in 1958, that a given ion actually has many resonant frequencies given by

$$\omega r=(2s+\beta)r/2$$

where s is any integer from $-\infty$ to $+\infty$, including $s=0$ but the other resonances can be important. Thus, the noise voltage between electrodes 10, 12 should not have a power spectrum extending above $r/2$, since some of these minor resonances corresponding to $s\neq0$ might reject the desired ions. This is the reason for the band pass filter 22. The purpose is to eliminate or considerably attenuate any of the higher or lower harmonics which could cause some of these minor resonances. The purpose of the band rejection filter should be apparent at this point. It is to eliminate or attenuate below an effective level, the frequency at which the desired ions resonate.

The advantage of applying field-producing signals of the type described herein to the mass spectrometer, is that the desired ion is strongly contained by the quadropole structure since operation which presumably is near the center of the a–q diagram shown in FIGURE 1, such as $a=0$ and $q=⅔$, is far from any unstable region. The purpose of the A.C. and D.C. voltage source 23 is to place the field and the structure at this operation point. The purpose of the noise signal and the filters is to further establish a field such that undesired ions are resonated and, thus, eliminated before reaching the target. As a result, much larger initial transverse velocities or displacement of ions on entrance into the field, than those permitted for standard "mass filter" operation with similar voltages is achieved.

There has accordingly been shown and described herein a novel, useful and improved method and means for operating a mass spectrometer of the types described.

What is claimed is:

1. In a mass spectrometer of the type having field establishing electrode structure comprising first, second, third and fourth elongated electrodes spaced from one another, parallel to one another and positioned to have a quadrupole relationship with one another, said first electrode being opposite said third electrode and said second electrode being opposite said fourth electrode, means for generating first signals for effecting a stable traversal of desired ions through the field established by said field establishing electrodes when said first signals are applied to said field establishing electrodes, said first signals comprising alternating current superimposed on direct current means for applying said first signals to said field establishing electrodes, means for generating a noise spectrum having a power spectral distribution over a predetermined range which excludes frequency components for which desired ions are resonant, and means for applying said noise spectrum signals to the first and third of said field establishing electrodes.

2. Apparatus as recited in claim 1 wherein said means for applying said noise signals to said field establishing electrodes includes a transformer having a primary winding to which said noise signals are applied and a center tapped secondary winding, and means connecting opposite ends of said center tapped secondary winding to said first and third elongated electrodes; said means for applying said first signals to said field establishing electrodes comprising a connection between said second and fourth elongated electrodes, and means connecting said first signal source to said connection and to the center tap of said secondary winding.

3. In a mass spectrometer of the type having a first, second, third and fourth elongated electrodes spaced parallel from one another in a quadrupole relationship, wherein both desired and undesired ions are injected into the region defined by said quadrupole electrodes for elimination by resonance therefrom of said undesired ions and for detection of said desired ions having a substantially axial traversal through said region, the improvement comprising means for establishing a field between said electrodes for enabling said desired ions to traverse said field substantially axially including a source of alternating current superimposed or direct current, and means for applying voltages from said source to all of said electrodes, and means for resonating out of said field all of said undesired ions comprising means for generating noise signals having a noise spectrum covering a power spectral distribution which has frequency components exclusive of those which cause resonance of said desired ions, and means for applying said noise signals to an opposed two of said electrodes.

4. The improvement in a mass spectrometer as recited in claim 3 wherein said means for applying said noise signals to two of said electrodes comprises a transformer having a primary winding to which said noise signals are applied and a center tapped secondary winding, said means connecting the outer ends of said center tapped secondary winding to said opposed two of said four electrodes; said means for applying said signals from said alternating current superimposed on a direct current source to said electrodes comprises a connection from said source to said secondary winding center tap, and another connection from said source to the remaining two of said four electrodes other than said opposed two.

5. In a mass spectrometer as recited in claim 3 wherein said means for generating noise signals with a noise spectrum having a power spectral distribution with frequency components omitting those at which the desired ion is resonant comprises means for generating noise signals, band pass filter means to which noise signals from said generator are applied, said band pass filter means having a band pass which passes therethrough all noise signals except those frequencies which are harmonically related to the frequency at which the desired ion is resonant, and a band rejection filter means to which the output of said band pass filter means is connected, said band rejection filter means rejecting the frequency at which said desired ion is resonant.

References Cited

UNITED STATES PATENTS

2,939,952	6/1960	Paul et al.	250—41.92
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RALPH G. NILSON, *Primary Examiner.*

W. F. LINDQUIST, *Assistant Examiner.*